Modulating the electric and magnetic properties of BiFeO₃ ceramics

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ABSTRACT

In this work, the electric and magnetic properties of BiFeO₃ (BFO) ceramics are modulated by changing the defect-dipoles using different Bi₂O₃ contents, where excessive Bi₂O₃ gives rise to the formation of iron (V_{Fe}) and oxygen (V_O) vacancies and Bi₂O₃ deficiency mainly leads to the formation of bismuth (V_{Bi}) and oxygen vacancies (V_O). It is of great interest to note that a rather low leakage current density can be achieved in both Bi₂O₃ deficient and excessive ceramics. We also find that a moderate level of Bi₂O₃ deficiency (< 9%) has little influence on d_{33} . Surprisingly, Bi₂O₃ excess, widely used for fabricating BFO ceramics with better properties in the past, cannot improve d_{33} . An enhanced piezoelectricity ($d_{33} = 49\text{--}51$ pC/N) can be obtained in the BFO ceramics with a wide Bi₂O₃ content range (i.e., $x = -0.09\text{--}0.09$). A large remanent polarization ($2P_r \sim 90\text{--}119$ $\mu\text{C}/\text{cm}^2$) and a tunable magnetization ($M_r = 0.022\text{--}0.038$ emu/g and $H_c = 0.87\text{--}4.04$ kOe) are achieved in BFO ceramics with $x = -0.15\text{--}0.15$. These defect-dipoles induced by Bi₂O₃ deficiency or excess can well modulate the electric and magnetic properties of BiFeO₃ ceramics.

1. Introduction

Multiferroic materials that simultaneously exhibit two or more than two ferroic order parameters are attracting great attention due to their intriguing fundamental physics and some potential applications [1–5]. Among them, bismuth ferrite (BiFeO₃, abbreviated as BFO) is one of the most well-known multiferroic materials due to its high Neel temperature ($T_N \sim 370$ °C) and high Curie temperature ($T_C \sim 825$ °C) [6]. In the past decades, extensive researches have been devoted to BFO because of its extremely giant spontaneous polarization ($P_s \sim 150$ $\mu\text{C}/\text{cm}^2$) and novel magnetoelectric coupling [2]. However, the easy formation of impurity phases (e.g., Bi₂Fe₄O₉ and Bi₂₅FeO₃₉) during BFO preparation, as well as the poor insulation and high coercive field properties, strongly restrain the development of BFO-based devices [7,8].

Ferroelectricity and magnetism are two important properties for BFO. Here, Fig. 1 lists some noticeable ferroelectricity studies in BFO. It can be found that a fully saturated P - E loop can be readily attained in BFO thin films, where their $2P_r$ mainly ranges from 100 to 292 $\mu\text{C}/\text{cm}^2$ and their E_c varies from 120 kV/cm to 470 kV/cm [9–14]. The flexible ferroelectricity is the result of intrinsic structure modification by the strain engineering. Specially, a remarkably giant remnant polarization ($2P_r \sim 292$ $\mu\text{C}/\text{cm}^2$) was achieved in tetragonal structure ($P4mm$: $a = 0.393$ nm and $c = 0.400$ nm) thin film deposited on Pt/TiO₂/SiO₂/Si substrates [9]. The large P_r was ascribed to the elastic constraints on lattice parameters and ionic displacements [9]. In BFO

single crystal, Lebeugle et al. reported that $2P_r$ was about 120 $\mu\text{C}/\text{cm}^2$ along [012] direction but this value would be larger along the [001]_{hex} direction [15]. Both thin films and single crystal can exhibit saturated ferroelectricity. However, up to now, it is still difficult to fabricate single-phase BFO-based ceramics with a well-saturated P - E loop using the conventional solid-state route. As shown in Fig. 1, $2P_r$ of the BFO-based ceramics is in the ranges of 22 to 66 $\mu\text{C}/\text{cm}^2$, and their E_c varies from 40 kV/cm to 130 kV/cm [16–23]. In fact, we assume that these reported P - E loops are not fully saturation, that is, some domains do not respond to the driving fields used in these reports. Previously, it was found that P - E loops of BFO ceramics were highly temperature and frequency dependent [24]. Therefore, they are the critical factors in obtaining a well-saturated P - E loop. Unfortunately, most of previous researches ignore the adjustment of measurement temperature and frequency. In addition, BFO is known for its high Curie temperature ($T_C \sim 825$ °C), but the piezoelectricity (d_{33}) of rhombohedral-phased BFO ceramics is usually lower than 40 pC/N [24]. It is found that the remanent magnetization of the BFO-based ceramics with good ferroelectricity ranges from 0.016 emu/g to 0.074 emu/g [5]. Therefore, the ferroelectricity, piezoelectricity and magnetism of BFO ceramics need to be further investigate.

It is known to all that the defect engineering plays an effective role in tailoring the properties of ceramics [25–30]. Defect-dipoles have been widely investigated in Pb-, BiNaTiO₃-, KNaNbO₃- and BaTiO₃-based ceramics because of their importance in aging, large electric-

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Fig. 1. The ferroelectricity of BFO single crystal, ceramics and thin films.

field-induced strain and domain dynamics [31,32]. In fact, defect-dipoles in the ceramics can cause the so-called “volume effect”, which could stabilize its P_s [32]. Additionally, these defect-dipoles are inclined to move to the domain walls, interact with the domain walls, and then impede their movements, which could obviously affect their ferroelectricity [26,33,34]. In addition, note that the E_C for BFO ceramics varies from 40 kV/cm to 130 kV/cm at room temperature [24,35]. And this highly dispersed E_C may be closely related to the presence of defect-dipoles in BFO ceramics. Previously, it was reported that the formation of intrinsic defects (e.g., V_{Bi} , V_O and V_{Fe}) could result in an enhancement of magnetic properties [2]. As a result, the existence of defect-dipoles could tailor both their ferroelectric and magnetic properties and then may contribute to the enhancement of magnetoelectric coupling effect in BFO ceramics. Moreover, the defects strongly affect the leakage current density in BFO bulks and an improper level of defects could lead to a poor insulation.

However, the research of defect-dipoles in BFO is still lacking. In this work, we explored the effect of defect-dipoles on the electric and magnetic properties in BFO ceramics. The components of $Bi_{0.95(1-x)}Sm_{0.05}Fe_{0.95}Sc_{0.05}O_3$ ($x = -0.15$ – 0.15) were selected. Here we illuminate some reasons why we choose Sm and Sc co-doping

in BFO. First, it was reported that the bond enthalpy of Sm–O (619 ± 13 kJ/mol) is much larger than Bi–O (343 ± 6 kJ/mol) [36], which could reduce the Bi volatilization during sintering. Second, Sc^{3+} is more stable than Fe^{3+} [24], which could impede valence fluctuation of iron ions ($Fe^{3+} - Fe^{2+}$). Third, a moderate co-doping of Sm and Sc could enhance the piezoelectricity and ferroelectricity in BFO ceramics [24].

2. Experimental procedures

The BSFSO- x ceramics were prepared by a modified rapid thermal quenching technique using high-purity powders of Bi_2O_3 (99%), Fe_2O_3 (99%), Sm_2O_3 (99.9%), and Sc_2O_3 (99.999%). These raw materials were produced by Sinopharm Chemical Reagent limited corporation (China). The initial materials were homogeneously mixed in alcohol using zirconia balls for about 24 h, and then were dried and pressed into disks of 10 mm in diameter and 1 mm in thickness. Finally, these samples were sintered at 820–880 °C for 5 min with a heating rate about 10 °C/min and followed by a quenching process from 600 °C to ambient temperature. Then, these samples were polished to 0.5 mm in thickness. Silver electrodes were pasted on both sides and were fired at 550 °C for 10 min. All samples were poled at a temperature of 100 °C in a silicon oil bath. And P - E loops were measured at a temperature of 100 °C in a silicon oil bath using a Radiant ferroelectric workstation. Then, thermal stability measurements were carried out. To do so, d_{33} was measured at room temperature after these samples were annealed at a scheduled temperature for 30 min with a heating rate of 3 °C/min.

The crystal structure of these ceramics was characterized by X-ray diffraction (XRD) (Bruker D8 Advanced XRD, Bruker AXS Inc., Madison, WI, CuK α). X-ray photoelectron spectroscopy (XPS) measurements were carried out with a spectrometer (VG ESCALAB220i-XL, Thermo Scientific, Surrey, UK) with Al K α radiation. Their cross-section micro-structure was analyzed using field emission-scanning electron microscopy (FE-SEM) (JSM-7500, Japan). Their piezoelectric constant (d_{33}) was measured by a piezo- d_{33} meter (ZJ-3 A, China). These P - E loops and leakage current density were measured using a Radiant workstation. The magnetization properties of the ceramics were measured at RT (~ 300 K) by a physical property measurement system (PPMS, Quantum Design) with VSM option.

Fig. 2. XRD patterns of the BSFSO- x ceramics, measured at (a) $2\theta = 20$ – 60° and (b) $2\theta = 30$ – 33° .

3. Results and discussions

3.1. Structure

Fig. 2(a) shows XRD patterns of the BSFSO-*x* ceramics, measured at $2\theta = 20\text{--}60^\circ$, and the enlarged XRD patterns with $2\theta = 30\text{--}33^\circ$ are shown in Fig. 2(b). It can be found that these ceramics with $x = -0.15\text{--}0.15$ exhibit a typical diffraction peak of *R*3c space group. However, Bi-rich impurity phases ($\text{Bi}_{25}\text{FeO}_{39}$, indexed by $\blacklozenge$) appears in the BSFSO-*x* ceramics with $x \geq 0.09$, and $\text{Bi}_{25}\text{FeO}_{39}$ contents increase with further increase of Bi_2O_3 content. Additionally, a Fe-rich impurity phase of $\text{Bi}_2\text{Fe}_4\text{O}_9$ (marked by ∇) is found in some Bi_2O_3 deficient samples [37]. Therefore, an excessive nonstoichiometric ratio of Bi_2O_3 and Fe_2O_3 may result in a formation of some impurity phases. Actually, these impurity phases cannot be avoided even in an homogeneous mixture of stoichiometric oxides due to the thermodynamic instability of BFO and its complex reaction kinetics [7]. It is of also interest to note that the XRD peaks shift towards a higher 2θ angle when x decreases from 0.03 to -0.15 and x increases from 0.03 to 0.15. This is due to the unit cell shrinking induced by the presence of bismuth and oxygen vacancies in Bi_2O_3 deficient samples as well as iron and oxygen vacancies in Bi_2O_3 excessive samples.

It is well known oxygen vacancies are inevitable in BFO ceramics fabricated by a conventional high-temperature sintering technique [24]. Figs. 3(a)–(e) demonstrate the XPS narrow scan of Fe 2p of BSFSO-*x* ceramics. The Fe 2p doublet contains two sub-peaks of $\text{Fe } 2p_{1/2}$ and $\text{Fe } 2p_{3/2}$. It can be found in Figs. 3(f)–(j) that Fe $2p_{3/2}$ can be further de-convoluted into two sub-peaks, implying the coexistence of Fe^{2+} and Fe^{3+} . The detailed fitting results are listed in Table 1. The existence of Fe^{2+} also implies the presence of oxygen vacancies in the ceramics [38]. In addition, the formation of Fe^{2+} can slightly alter the magnetization of BFO [2].

Ferroelectricity and dielectric properties of BFO-based ceramics are strongly dependent on their grain morphology [39,40]. Fig. 4 displays the cross-section FE-SEM images of the BSFSO-*x* ceramics. It can be found that the grain morphology of Bi_2O_3 excessive samples is quite different from the Bi_2O_3 deficient ones. The Bi_2O_3 excessive samples have a larger grain size and a more regular shape than Bi_2O_3 deficient samples. Meanwhile, the bulk density of all components is also displayed in Fig. 4. One can notice that samples with Bi_2O_3 excess also possess a larger density than the ones with Bi_2O_3 deficiency. The existence of impurity phases may be part of the reason. Because the density of Bi-rich impurity phase (e.g., $\text{Bi}_{25}\text{FeO}_{39}$) is larger than Fe-rich

Table 1

Quantitative analysis of Fe $2p_{3/2}$ XPS sub-peaks.

<i>x</i>	Peaks	FWHM/eV	Area (P) CPS.eV	Atomic %
<i>x</i> = 0.15	709.58	2.77	11,426	72.5
	711.88	2.77	4331	27.5
<i>x</i> = 0.09	709.15	2.77	23,171	76.7
	711.59	2.77	7030	23.3
<i>x</i> = 0	709.12	2.77	23,193	23.7
	711.48	2.77	7209	76.3
<i>x</i> = -0.09	709.14	2.77	13,948	73.8
	711.51	2.77	4949	26.2
<i>x</i> = -0.15	709.64	2.77	3294	70.0
	711.96	2.77	1409	30.0

impurity phase (e.g., $\text{Bi}_2\text{Fe}_4\text{O}_9$). Generally, all these specimens exhibit a dense microstructure even the sintering time being as short as 5 min. Previously, most of the works reported in BFO-based ceramics used a much longer sintering time (> 5 min), which seems to be redundant and even harmful, because further annealing can increase the Bi and O loss and cause the decomposition of BFO [7].

3.2. Electric properties

Fig. 5 displays the leakage current density versus applied electric field (*J-E*) of the BSFSO-*x* ceramics up to ± 50 kV/cm at room temperature (RT). One can see that the magnitudes of *J* are comparable to those in 10% Ti-doped BFO bulks [41]. The low *J* in Bi_2O_3 -deficient samples indicates that Bi_2O_3 volatilization during sintering may not be the main reason for the poor insulation property in BFO-based ceramics [42]. Recently, Qiang et al. reported that bismuth vacancies have lower defect formation energy than oxygen vacancies under typical laboratory conditions [43]. Therefore, the easy formation of bismuth vacancies can result in a p-type semiconductor [44], where the defect reaction can be written as [44]:

where $\text{V}_{\text{Bi}}^{\bullet\bullet}$ and $\text{h}^{\bullet}$ are bismuth vacancy and hole, respectively.

Generally, the existence of holes will significantly improve the conductivity of BFO ceramics. However, the formation of oxygen vacancies can compensate the holes generated by bismuth vacancies, where the defects reaction can be modified as:

where $\text{V}_{\text{O}}^{\bullet\bullet}$ represents oxygen vacancy.

The drastic decrease in hole's density can result in an overall

Fig. 3. High-resolution X-ray photoelectron spectroscopy of BSFSO-*x* ceramics of Fe 2p, (a) $x = 0.15$, (b) $x = 0.09$, (c) $x = 0$, (d) $x = -0.09$, (e) $x = -0.15$. The XPS fitting spectra of Fe $2p_{3/2}$ narrow scan spectra, (f) $x = 0.15$, (g) $x = 0.09$, (h) $x = 0$, (i) $x = -0.09$, (j) $x = -0.15$.

Fig. 4. Cross-section FE-SEM images of the BSFSO- x ceramics; (a) $x = 0.15$, (b) $x = 0.09$, (c) $x = 0$, (d) $x = -0.09$, (e) $x = -0.15$.

increase of the insulating property. As a result, these BFO ceramics with Bi_2O_3 deficiency deliberately designed may contain a comparable amount of bismuth vacancies and oxygen vacancies, which could also result in a low J . Moreover, as shown in Fig. 5(b), J reaches its minimum value of $\sim 10^{-7}$ A/cm² in the sample with $x = 0$ at 50 kV/cm. The J slightly increases in both Bi_2O_3 excessive and deficient samples. In addition, J reaches about 1×10^{-6} A/cm² in the BSFSO- x ceramics with higher Bi_2O_3 deficiency (e.g., $x \leq -0.15$) and Bi_2O_3 excess (e.g., $x \geq 0.09$). The slightly increase in J in the Bi_2O_3 deficient/excessive samples may be ascribed to the presence of these impurity phases or increased defects contents in the materials [45]. As shown in Fig. 5(c), the slopes of $\log J$ versus $\log E$ for the samples with $x = 0.03$ and $x = 0.09$ are about 1.08 and 1.18, respectively, which is in good agreement with Ohmic conduction mechanism. However, the slope of $\log J$ versus $\log E$ for the samples with $x = 0.15$, -0.03 and -0.09 is

2.03, 2.06 and 2.05, respectively, which is consistent with the space-charge-limited current conduction (SCLC) mechanism.

It was reported that Bi_2O_3 volatilization could be responsible for the lower d_{33} of BFO ceramics [7]. However, as shown in Fig. 6(a), there are no significant changes in d_{33} for the samples with $x = -0.09$ – 0.09 , which means that Bi_2O_3 excess cannot help improve d_{33} and slight Bi_2O_3 loss does not decrease d_{33} . It is known that the piezoelectric coefficient (d_{33}) contains the contributions from the intrinsic/lattice behavior of the material, domain walls motion and other extrinsic factors, of which domain walls motion plays a major role and contribute to about 70% of the total macroscopic piezoelectric response [46]. As shown in Fig. 4, the grain sizes of the Bi_2O_3 -deficient samples are smaller than those of the Bi_2O_3 excessive ones. And smaller grain size results in smaller domain size and could lead to an increased d_{33} due to the enhancement in the extrinsic contribution [47,48]. Additionally,

Fig. 5. (a) Leakage current density of the BSFSO- x ceramics as a function of applied electric field in the BSFSO- x ceramics at room temperature (RT); (b) J at 50 kV/cm as a function of x ; (c) $\log J$ versus $\log E$ and the fitted curves.

Fig. 6. (a)–(c) d_{33} , ϵ_r and $\tan \delta$ of the BSFSO- x ceramics, measured at 1 kHz and room temperature. (d) Thermal stability of normalized d_{33} of BSFSO- x ceramics.

Table 2

Electrical parameters of the BSFSO- x ceramics at different frequencies.

x	f (Hz)	E_c (kV/cm)	E_t (kV/cm)	$2P_r$ ($\mu\text{C}/\text{cm}^2$)	d_{33} (pC/N)
0.15	0.5	67.1	5.0	89	26
	10	66.9	19.4	38	20
0.09	0.5	64.4	3.8	90	30
	10	67.3	14.2	46	20
0.03	0.5	62.8	7.8	47	20
	10	65.6	15.8	32	16
0	0.5	66.2	11.3	44	18
	10	69.3	19.3	29	10
-0.03	0.1	76.0	3.5	26	19
	10	72.7	26.4	11	11
-0.09	0.1	95.0	3.6	25	14
	10	59.3	16.9	4.4	5.3
-0.15	0.1	84.5	-0.7	119	33
	10	67.6	10.0	10.7	13

the electrically switchable P_D originated from defect-dipoles could also contribute to an increased d_{33} [49]. As a result, a moderate level of Bi_2O_3 deficiency may not lead to a poor d_{33} . In addition, the rather low leakage current density is also crucial for the enhanced d_{33} . Because a high insulation property is a guarantee for obtaining a fully poled sample. However, d_{33} dramatically decreases in the samples with Bi_2O_3 excess or deficiency level higher than 9%, which may be due to the increase of the impurity phases content. In addition, it is found that the poling behavior of these ceramics strongly depends on Bi_2O_3 content. The poling electric field (E_p) of $x = -0.09$ is about 90 kV/cm under 100 °C, whereas E_p drops to 50 kV/cm for $x = 0$ and 40 kV/cm for $x = 0.15$. So it implies that domain walls are significantly pinned in the Bi_2O_3 deficient samples [50]. In addition, domain wall mobility can also be affected by the reduction in grain size, especially the non-180° domain walls [51,52]. The decrease in grain size could also contribute to the increase in E_p . Interestingly, according to E_c in Table 2, the Bi_2O_3 excessive samples could be fully poled even under a field blow E_c .

Dielectric properties are crucial for evaluating the electrical performance of ceramics. Figs. 6(b) and (c) show the dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of the BSFSO- x ceramics, measured at RT and 1 kHz. Their dielectric properties are highly modulated by Bi_2O_3

content [53]. The ϵ_r increases with the Bi_2O_3 level, and ϵ_r (~92) of the ceramics with $x = 0.15$ is more than two times larger than that of the ones with $x = -0.15$ (~39). The clamped domain walls can reduce ϵ_r [54]. Actually, a large portion of ϵ_r originates from the extrinsic contributions which is rather complex [40,55]. Therefore, it is difficult to give a reasonable explanation to the variation in ϵ_r at the present stage of research. Moreover, one can note that $\tan \delta$ of the samples is all < 2% under 1 kHz comparable to the insulating BLFTO reported previously [56]. Especially, $\tan \delta$ reaches the minimum value for the sample with $x = 0$. One can observe that the ceramics with $x = -0.15$ exhibit a lower $\tan \delta$ with respect to the ones with $x = 0.03$. It was previously reported that $\tan \delta$ was mainly caused by the extrinsic contribution (i.e., domain walls motion) because of mechanical friction, and then pinned domain walls can result in a lower $\tan \delta$ [40,57]. In addition, these impurity phases could also increase $\tan \delta$, and then it is not a surprise that the minimum $\tan \delta$ (~0.57%) is achieved in the ceramics with $x = 0$. From the point view of applications, thermal stability of piezoelectricity is of great importance. One can notice from Fig. 6(d) that the curves of all the samples are highly similar, confirming that the depolarization temperature (T_d) is just slightly dependent on Bi_2O_3 content. Interestingly, their d_{33} retains about 30% under an annealing temperature of 750 °C, indicating the Curie temperature (T_C) must be higher than 750 °C.

Figs. 7(a)–(g) show the P - E loops of the BSFSO- x ceramics, measured at 10 Hz and 100 °C. Fig. 7(h) displays the variation in $2P_r$, E_c , E_t and d_{33} , and Fig. 7(i) demonstrates the P - E loops under a comparable electric field (120 kV/cm). Generally, these samples with excessive Bi_2O_3 exhibit well-saturated P - E loops, whereas the Bi_2O_3 deficient ones show more slant P - E loops. Especially, Bi_2O_3 -deficient ceramics with $x = -0.03$ still exhibit a slant P - E loop even under a high driving field of 160 kV/cm. Additionally, there is no significant change in E_c except for the ones with $x = -0.03$, as shown in Fig. 6(h). However, it was found that the E_c with $x = -0.09$ and $x = -0.15$ is lower than the one with $x = -0.03$ because the P - E loops of $x = -0.09$ and -0.15 are far from fully saturated, which means that their E_c did not reach their maximum values at this condition. More importantly, one can notice that all these P - E loops are asymmetric, implying the existence of an internal bias field (E_i). And the E_i can be simply calculated by the equation ($E_i = |(E_c^+ + E_c^-)|/2$) in depinned P - E loops [58]. We

Fig. 7. (a)–(g) P - E loops of the BSFSO- x ceramics, measured at 10 Hz and 100 °C, (h) P_r , E_c , E_i and d_{33} of the P - E loops, (i) P - E loops of the BSFSO- x ceramics measured at 120 kV/cm.

argue that this E_i mainly originates from defect-dipoles in the BSFSO- x ceramics. In Bi_2O_3 deficient bulks, Bi_2O_3 deficiency causes the formation of bismuth and oxygen vacancies, and the defect equation can be written as:

Correspondingly, bismuth and oxygen vacancies could form $\text{V}_{\text{Bi}}^{\prime\prime}$ - $\text{V}_{\text{O}}^{\prime\prime}$ defect-dipoles. In addition, oxygen vacancies could induce the presence of Fe^{2+} and then $\text{Fe}_{\text{Fe}}^{2+}$ - $\text{V}_{\text{O}}^{\prime\prime}$ defect-dipoles can be also formed. Additionally, in the Bi_2O_3 excessive samples, iron and oxygen vacancies can be generated. The defect equation can be written as:

The coexistence of $\text{V}_{\text{Fe}}^{\prime\prime}$ and $\text{V}_{\text{O}}^{\prime\prime}$ could lead to the formation of $\text{V}_{\text{Fe}}^{\prime\prime}$ - $\text{V}_{\text{O}}^{\prime\prime}$ defect-dipoles. Moreover, one can notice that P_r gradually increases with the increase in Bi_2O_3 content. And $2P_r$ of the ceramics with $x = 0.09$ reaches $46 \mu\text{C}/\text{cm}^2$ under a driving field of 120 kV/cm. In contrast, the ceramics with $x = -0.03$ demonstrates a low $2P_r$ ($11 \mu\text{C}/\text{cm}^2$) at 160 kV/cm. It is believed that the giant P_s in BFO is originated from the large relative displacement between Bi and O ions induced by the high stereochemical activity of $6s^2$ lone pair of Bi^{3+} [59]. Therefore, Bi_2O_3 deficiency leads to the formation of bismuth vacancies and consequently a decrease in P_r . The smaller grain size of the Bi_2O_3 -deficient bulks could be another reason for the decrease in P_r due to the domain clamping effect from the neighboring grains [40,55]. Fig. 7(h) shows the P - E loops of the BSFSO- x ceramics, measured at a comparable electric field of 120 kV/cm. It can be seen that $2P_r$ also reaches its

maximum value in the ceramics with $x = 0.09$.

The P - E loops of the BFO-based ceramics are strongly temperature and frequency dependent [24,58]. The domains in BFO-based ceramics are difficult to be fully reversed due to its high coercive field. The frequency dependence of P - E loops are shown in Fig. 8, and the corresponding electrical parameters are listed in Table 2. It can be found that E_i is dramatically diminished at a lower frequency, revealing that defect-dipoles can respond to the driving fields under lower frequencies. Previously, it was reported that oxygen vacancies are highly mobile while cation vacancies are relatively more stable [32,60]. Therefore, the easy movement of oxygen vacancies should be the main reason for the decrease in E_i . Meanwhile, P_r significantly increases due to more involvement of domain reversal. It is worth mentioning that $2P_r$ reaches as high as about $90 \mu\text{C}/\text{cm}^2$ for the one with $x = 0.09$ under a frequency of 0.5 Hz [24]. One notices that the P - E loops measured at a low frequency contain some contribution from leakage current. Moreover, it is well known that a close relationship between piezoelectric coefficient and polarization exists, that is, $d_{33} = 2Q_{11}\epsilon_0\epsilon_{33}P_3$, where P_3 is the polarization along polar axis [61]. Therefore, we listed d_{33} of all the samples after P - E measurements. Correspondingly, one can notice that their d_{33} is still much lower than those of the fully poled bulks under a DC field. So it is difficult to reverse all the domains under such a frequency, temperature and excitation field. Besides, their E_c increases with the increase in measurement frequency [58]. Herein, it can be found that E_c increases at lower frequencies, indicating that P - E loops of

Fig. 8. Frequency dependence of P - E loops for the BSFSO- x ceramics, measured at 100 °C; (a) $x = 0.15$, (b) $x = 0.09$, (c) $x = 0.03$, (d) $x = 0$, (e) $x = -0.03$, (f) $x = -0.09$, (g) $x = -0.15$.

the Bi_2O_3 deficient samples under 10 Hz is far from well-saturated. Most of the domains do not respond to the driving field and remain pinned by defect-dipoles. Curiously, the $2P_r$ reaches $119 \mu\text{C}/\text{cm}^2$ at the driving field of 120 kV/cm with a frequency of 0.1 Hz. But the contribution from the leakage is also large. Moreover, the d_{33} after the P - E measurement with a frequency of 0.1 Hz is about 33 pC/N, which is nearly saturated. This indicates that almost all the domains in BFO ceramics with $x = -0.15$ could respond to the driving field under this condition.

3.3. Magnetic properties

Magnetoelectric coupling in BFO have attracted considerable attention [62,63]. It is known that bulk BFO exhibits a G-type antiferromagnetic order and has a low M_r ($\sim 10^{-4}$ emu/g) [37,64–66]. However, Paudel et al. found that the effect of intrinsic defects on magnetism was also complex by using the first-principles calculations, where the V_{Bi}'' , V_{O}' and V_{Fe} can induce a magnetic moment of $1 \mu_B$, $1 \mu_B$ and $5 \mu_B$ per vacancy, respectively, while V_{O}'' and V_{O} cannot generate any magnetic moment [2]. Additionally, it was reported site engineering could result in an enhancement in the sample's magnetization [67–69].

The magnetization hysteresis (M - H) loops at RT (300K) are shown in Fig. 9. The remanent magnetization ($M_r = 0.038$ emu/g) and coercivity ($H_c = 4.04$ kOe) reached the maximum value in the one with $x = 0$. Previously, it was reported that the BFO ceramics with 5% Sc-doping

show a rather low M_r of 0.71 memu/g [70]. Therefore, the enhancement in M_r of BSFSO could be attributed to Sm-doping or the formation of intrinsic defects, which could lead to the collapse of space-modulated spin structure [67,68]. In addition, the formation of Fe^{2+} can cause a double exchange interaction between Fe^{3+} and Fe^{2+} , leading an enhancement in their magnetic properties [71]. Then a slight decreased magnetization ($M_r = 0.036$ emu/g) was measured in the one with $x = 0.15$. The H_c increases from 2.57 kOe (at $x = -0.15$) to 4.04 kOe (at $x = 0$) and then decrease to 0.87 kOe (at $x = 0.15$). The higher H_c also denotes that the enhancement in the sample's magnetization is not from Fe_2O_3 impurity, as the H_c of Fe_2O_3 is lower than 100 Oe [67]. In addition, the formation of paramagnetic $\text{Bi}_2\text{Fe}_4\text{O}_9$ may be responsible for the reduction in M_r in the Bi_2O_3 deficient samples.

4. Conclusion

In this work, defective BFO-based ceramics with different Bi_2O_3 contents are successfully prepared by a modified rapid thermal quenching technique. The effects of Bi_2O_3 contents on the phase structure, microstructure, piezoelectric, ferroelectric and magnetic properties are systematically investigated. All the samples exhibit a low leakage current density at RT. A moderate Bi_2O_3 loss has little influence on the magnitude of d_{33} , and Bi_2O_3 excess cannot enhance d_{33} . The samples with Bi_2O_3 deficiency show a slant P - E loop together with higher E_c and lower P_r due to the restriction of domain walls motion induced by smaller grain size and defect-dipoles. Importantly,

Fig. 9. (a)–(e) Magnetic hysteresis loops of the BSFSO- x ceramics at RT; The composition dependence of (f) remanent magnetic (M_r) and (g) coercivity (H_c).

the ceramics with $x = 0.09$ show an unsaturated P - E loop with a giant remanent polarization ($2P_r \sim 90 \mu\text{C}/\text{cm}^2$). Additionally, a tunable magnetization ($M_r = 0.022\text{--}0.038 \text{ emu/g}$) is also achieved.

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